Martensite-based stainless steel OCTG of 15Cr-based and 17Cr-based material for sweet and mild sour condition.

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Summary

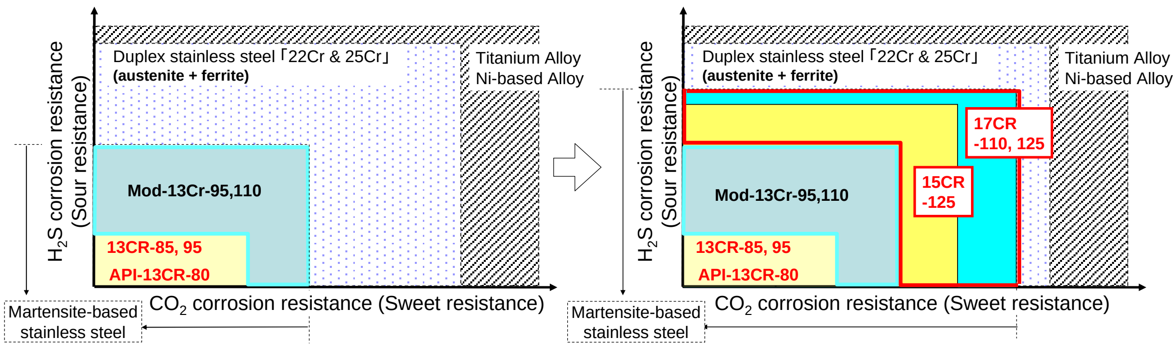
This report mentions the concept of the alloy design and the updated corrosion data about martensite-based stainless steel OCTG materials of 15Cr (generic 15Cr-6Ni-2Mo) and 17Cr (generic 17Cr-4Ni-2.5Mo-Cu-W). These materials aim at the corrosion environment between modified-13Cr stainless steel OCTG (generic 13Cr-4Ni-1Mo and 13Cr-5Ni-2Mo) and duplex stainless steel OCTG of 22Cr and 25Cr, and are also expected to expand the application area even to the milder corrosion environment region of duplex-stainless-targeting area. In other words, they are positioned as the upper grade of Modified-13Cr, and also as alternatives in the milder corrosion region for duplex-stainless-targeting area. Yield strength level of 15Cr (generic 15Cr-6Ni-2Mo) is 125ksi-grade, and the one of 17Cr (generic 17Cr-4Ni-2.5Mo-Cu-W) is 110ksi-grade and 125ksi-grade. The alloy-design concept is mentioned below, and both the corrosion-resistant and mechanical properties are discussed in details below.

1 Introduction

As stainless steel OCTG materials for severe sweet application, L80-13Cr in API-5CT and its related lineups of 85ksi-grade and 90ksi-grade 13Cr (referred as “API-13Cr” as a whole) have been widely known and used in oil and gas fields. Modified-13Cr (referred as “Mod-13Cr”) OCTG materials[1-4], which is 13Cr-based martensitic stainless steel with Ni and Mo addition, has also been applied for more severe sweet environment and/or sweet and mild sour conditions. In this paper, 15Cr[5] (generic 15Cr-6Ni-2Mo: referred as “15CR”), and 17Cr[6,7] (generic 17Cr-4Ni-2.5Mo-Cu-W: referred as “17CR”) are reported and discussed as higher-grade martensite-including stainless steel OCTG materials in yield strength and in corrosion-resistant properties than Mod-13Cr and API-13Cr.
Figures 1-(a) and 1-(b) are schematic diagrams to show expected targeted corrosion environment for 15CR and 17CR as parameters of CO_2 and H_2S conditions. These materials target at the severer corrosion environment in CO_2 and H_2S than Mod-13Cr and API-13Cr. To be precise, as shown in Figure 1-(a), the upper area (the severer area) of Mod-13Cr used to be, or still be the area intended for duplex stainless steel. 15CR and 17CR aim at corrosion regions as shown schematically in Figure 1-(b). That is, they are intended for the corrosion area over Mod-13Cr-targeting area, and the lower area (the milder area) that duplex stainless steels still aim at. When viewed from a different angle, 15CR and 17CR can be positioned as alternative options for duplex stainless steels of 22Cr and 25Cr, especially in the lower region (the milder region) of their targeting corrosion environment.

2 Alloy design concept and strength grade

The alloy design concept is mainly based on two things. One is to enhance the stability of passive film to improve corrosion resistant properties by adding corrosion-resistant alloy elements of Cr, Mo, Ni, Cu and so on. This concept is widely common in corrosion-resistant alloys (CRAs), including duplex stainless steel and Ni-alloys.



(a) Conventional image in corrosion resistance properties for stainless steel OCTG application

(b) Expected application area for 15CR and 17CR stainless steel OCTG

Figure 1: Schematic diagrams to show expected targeted corrosion environment for 15CR and 17CR as parameters of CO_2 and H_2S conditions: (a) Conventional image in corrosion resistance properties for stainless steel OCTG application and (b) Expected application area for 15CR and 17CR

The other is to keep martensite as a main phase for the origin of strength in stainless steel. This second concept is markedly contrast with CRAs of duplex stainless steel and Ni-alloys, which are composed mainly of austenite phase and consequently depend on cold-drawing-based dislocation-strengthening.

These two characteristics are explained more explicitly by using Figure 2, which plots stainless steel OCTG materials on Schaeffler diagram, in which alloy elements are categorized as ferrite-stabilizing-elements (Cr, Mo etc.) of the horizontal direction and as austenite-stabilizing-elements (Ni etc.) of the vertical direction. It should be noted that Figure 2 is a kind of schematic diagram and does not academically have strict validity, because Schaeffler diagram is based on welding-based rapid cooling pattern, but, in contrast, stainless steel OCTG materials are produced in Quenching and Tempering basis or in Normalization and Tempering basis.

As for the alloy design of 15CR, the one of API-13Cr and Mod-13Cr is followed by 15Cr (diagonally right upward direction). That is, both ferrite-stabilizing-elements and austenite-stabilizing-elements are monotonically increased up to nearly below the boundary of austenite transformation. The chemical composition is optimized as 15Cr-6Ni-2Mo-Cu-based stainless steel. In contrast, the alloy design of 17CR is different from the traditional “monotonous addition” style. Ferrite-stabilizing-elements are increased as usual, but austenite-stabilizing-elements are reduced to keep martensite as main phase (diagonally right downward direction). If both elements are increased beyond the boundary of austenite transformation, a stainless steel with such chemical compositions changes into austenite stainless steel and then yield strength sharply drops due to martensite-free. Therefore, Ni-equivalent elements, especially Ni contents, are reduced to keep martensite as main phase. The chemical composition of 17CR is optimized as 17Cr-4Ni-2.5Mo-Cu-W-based stainless steel.

Yield strength in 15Cr is 125ksi-grade (861MPa-grade), and in 17Cr is 110ksi and 125ksi-grade (758MPa-grade and 861MPa-grade). The strength of both steels is based mainly on martensite, but not on cold-drawing-based dislocation-strengthening as duplex stainless steel is always based on.

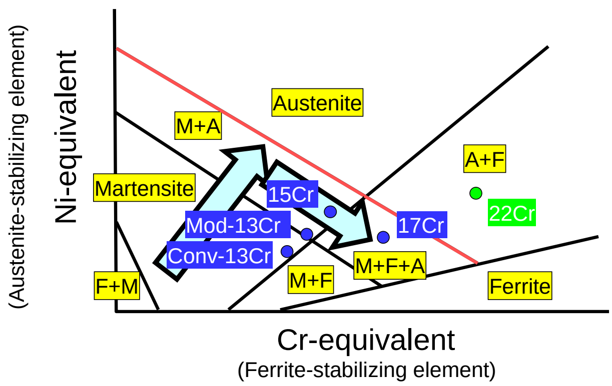


Figure 2: Stainless steel OCTG chemistry on Schaeffler diagram.

Table 1: 15CR and 17CR samples with comparative materials of other stainless steels.

Sample	Phase		UNS No	Chemical compositions	YS grade
17CR	Martensite-based	M+F (+A)	-	17Cr-4Ni-2.5Mo-1W-1Cu-LowC	110ksi- and 125ksi-grade
15CR		M (+A)	S42625	15Cr-6Ni-2Mo-1Cu-LowC	125ksi-grade
Mod-13Cr		M (+A)	-	13Cr-5Ni-2Mo-LowC	Comparative materials
API-13Cr		M	S42000	13Cr-0.2C	
22Cr	Duplex	A+F	S31803	22Cr-5Ni-3Mo-N (cold-drawn)	
25Cr		A+F	S32250	25Cr-7Ni-4Mo-N (cold-drawn)	

3 Experimental Procedure

15CR and 17CR are reported below in mechanical properties and in corrosion-resistant properties from the following viewpoints. Their properties are compared with other stainless steels of API-13Cr, Mod-13Cr and duplex stainless steels.

Table 1 shows the samples used for experiments under the category of chemistry, phase and yield strength level. As for 15CR, the chemical composition is 15Cr-6Ni-2Mo-Cu-based stainless steel, and it is composed mainly of martensite. The yield strength is 125ksi-grade. As for 17CR, the chemical composition is 17Cr-4Ni-2.5Mo-Cu-W-based stainless steel. As shown in Figure 2, it is composed mainly of martensite and a certain amount of ferrite with a small portion of austenite. Roughly saying, the volume ratio of martensite, ferrite and austenite is about 6-3-1. The yield strength is 110ksi-grade and 125ksi-grade. Both 15CR and 17CR stainless steel samples used in this report were based on mill-produced materials.

15CR and 17CR are evaluated from the following viewpoints of mechanical properties and of corrosion-resistant properties in the following ways;

3.1 Microstructure by optical micrograph

15CR and 17CR were observed at transversal cross-section with optical microscope after they were resin-embedded, polished and etched by Villella etchant. Samples were picked out from 15CR-125ksi-grade and 17CR-110ksi-grade.

3.2 Fracture toughness by Charpy impact test

Charpy impact test samples were taken from 15CR-125ksi-grade and 17CR-110ksi-grade in the form of 10mm X 5mm (half size) with V-notch of radius 2mm along longitudinal direction.

3.3 High-temperature yield strength and tensile strength (de-rating mechanical properties as a parameter of temperature)

Tensile test samples were taken along longitudinal direction from 125ksi-grade samples from 15CR and 17CR to carry out tensile test at elevated temperature from room temperature (referred as “RT”). 25Cr was also evaluated for comparison between martensite-based and duplex (austenite-ferrite-based) stainless steel. The range of tested temperature is from RT to 250 deg.C for 15CR and 17CR, and from RT to 200 deg.C for 25Cr.

3.4 Corrosion rate in high-pressured CO_2 corrosion

CO_2 corrosion properties were evaluated and compared by corrosion rate among API-13Cr, Mod-13Cr, 15CR and 17CR in 20%NaCl solution at the parameters of CO_2

partial pressure from 0.3MPa to over 10MPa and temperature form RT to 250deg.C, which targets at corrosion-resistant properties for severe sweet corrosion environment. The corrosion resistance in CO_2 corrosion was judged by using “0.127mm/year (= 5mil/year)” as the upper limit of application criteria.

3.5 SSC resistance

The SSC resistance data is updated in 15Cr-125ksi-grade, 17Cr-125ksi-grade and 17Cr-110ksi-grade by using proof-ring tests at RT in ambient pressure under the corrosion-related parameters of applied stress, pH, pH2S (balanced with CO2) and Cl- ion concentration.
For 15Cr-125ksi-grade, SSC resistance was evaluated with 100%SMYS under the corrosion-related parameters of pH, pH_2S (balanced with CO_2) and chloride ion concentration (1000ppm (0.165%NaCl), 20,000ppm (3.3%NaCl) and 121,200ppm (20%NaCl)) by using “NaCl + 5g/L CH_3COOH + pH-adjusted by CH_3COONa”. It should be noted that these 15Cr samples are composed of some kinds of specimens with different YS within specification range of 125 to 150ksi.
For 17Cr-125ksi-grade, SSC was assessed in comparison with the application limit of 15Cr-125ksi-grade in 20%NaCl solution, by using the sample with 134MPa of YS. The SSC tests were performed with 90%AYS under the corrosion-related parameters “20%NaCl solution + 5g/L CH_3COOH + pH-adjusted by CH_3COONa”.
For 17Cr-110ksi-grade evaluation, SSC resistance was evaluated in comparison with the application limit of SSC data for 17Cr-125ksi-grade in 20%NaCl solution. At the SSC test of 0.165%NaCl (1000ppm Cl-) solution, the test condition was based on 90%SMYS and “5g/L CH_3COOH + pH-adjusted by CH_3COONa”. In the case of the SSC test of 3.3%NaCl (20,000ppm Cl-) solution, it was performed at 90%SMYS through the adjustment of pH by using CH_3COOH + 0.41g/L CH_3COONa. At the SSC test of 20%NaCl (121,200ppm Cl-), the test condition was based on 90%AYS and “5g/L CH_3COOH + pH-adjusted by CH_3COONa”.

3.6 Pitting resistance

Pitting potentials were measured in 15CR and 17CR, together with comparative samples of Mod-13Cr (generic 13Cr-5Ni-2Mo-based). The pitting potential is defined as the voltage at current density of 100μm/cm^2 in ambient pressure at 25 deg.C in anodic polarization measurement. The corrosion environment is based on the three conditions; (1)0.165%NaCl solution (1000ppm of Cl- ion) in 100%CO_2, (2)20%NaCl solution (120,000ppm of Cl- ion) in 100%CO_2 and (3)20%NaCl solution (121,200ppm of Cl- ion) in 10%H_2S and 90%CO_2. In addition, these data were also plotted to pitting index (Cr+3Mo+16N).

3.7 Corrosion at low pH (acidizing simulation without inhibitors)

Corrosion properties were compared among Mod-13Cr, 15Cr, 17Cr and duplex stainless steels of 22Cr and 25Cr. The corrosion environments are intended for live acid condition and spent acid condition. The real acidizing is carried out by using inhibitors, but the tests were performed without any inhibitors to evaluate under an exaggerated condition. The former one was 15%HCl solution at 80deg.C in ambient pressure without any inhibitors, and the latter one was 25%NaCl solution at 80deg.C in ambient pressure of 100%CO_2 (0.1MPa of CO_2) at both pH 1.0 and pH2.0 by adjusting with HCl. After the test, the samples were evaluated by corrosion rate and cross-sectional optical micrograph.

4 Results

4.1 Microstructure by optical micrograph

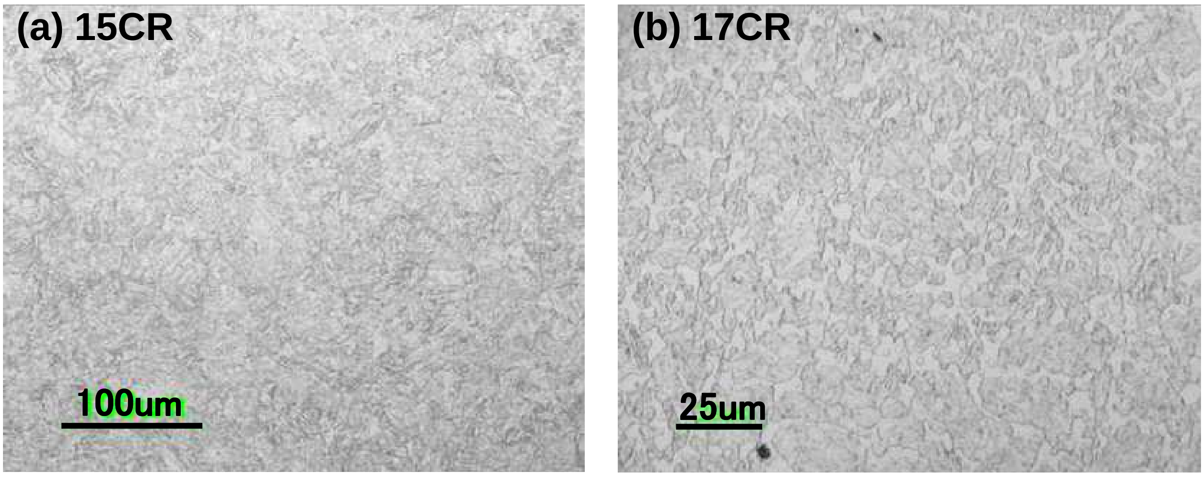


Figure 3: Optical micrographs of (a)15CR and (b)17CR.

Figures 3-(a) and 3-(b) show the optical micrographs of 15CR and 17CR, respectively. It should be noted that both micrographs are images at different magnification. 15CR is composed of martensite, and so it looks uniform microstructure. In contrast, 17CR is occupied mainly with martensite as gray area and secondly with ferrite as white area. Although both 15Cr and 17Cr include a small amount of austenite, it is difficult to observe it with optical micrographs. Finely-dispersed austenite can be detected, for example, with XRD.

4.2 Fracture toughness by Charpy impact test

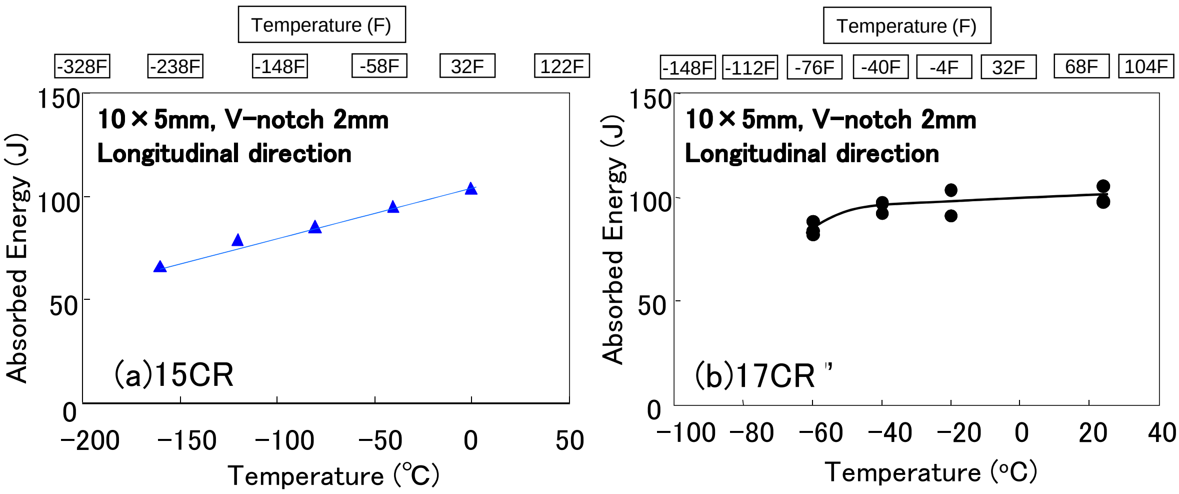


Figure 4: Fracture toughness at Charpy V-notch impact test of (a)15CR and (b)17CR.

Figures 4-(a) and 4-(b) show fracture toughness (absorbed energy) data as a parameter of temperature in (a)15CR and (b)17CR, respectively. Both samples have good toughness data, for example, around 100J at -40deg.C for 15CR and around 100J at -40deg.C for 17CR.

4.3 High-temperature yield strength and tensile strength (de-rating mechanical properties as a parameter of temperature)

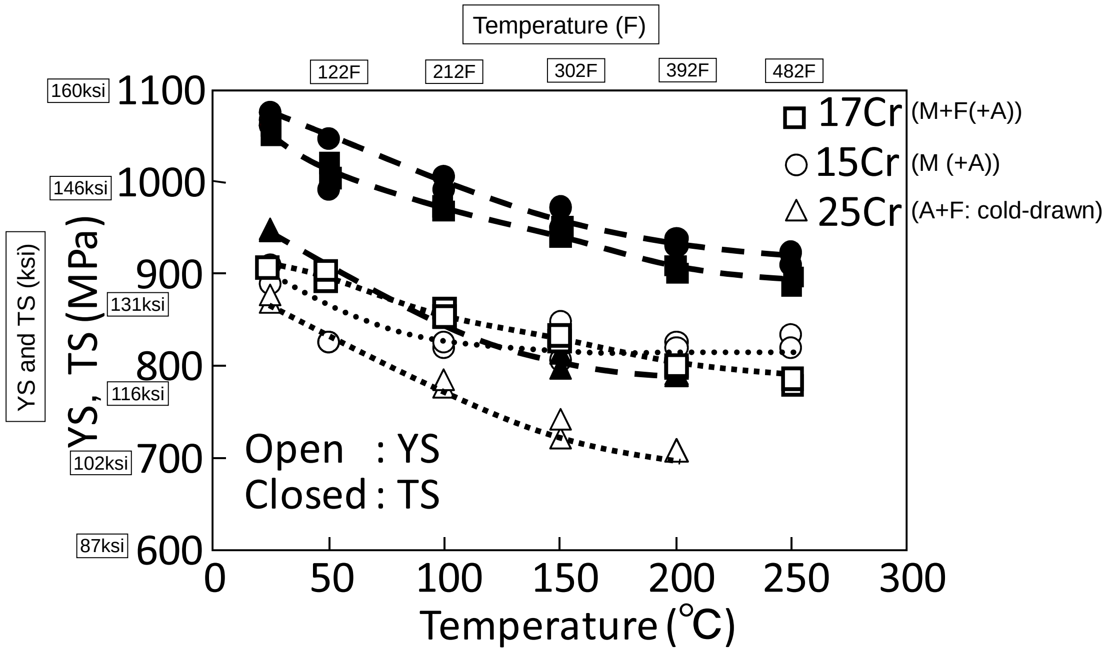


Figure 5: Yield strength and tensile strength vs. temperature in 15CR, 17CR and 25Cr with same yield strength at room temperature of around 125ksi (around 900MPa).

Figures 5 is the plot of yield strength (referred as "YS") and tensile strength (referred as "TS") versus elevated temperature in 15CR, 17CR and 25Cr. These three samples have the same yield strength at room temperature of around 125ksi (around 900MPa). As mentioned in Section 2, 15CR and 17CR are mainly composed of martensite, and so the strength in both steels are based on martensite. In contrast, duplex stainless steel is composed of austenite and ferrite. These microstructures in duplex stainless steel do not have strength, and cold-drawing-based dislocation strengthening is needed to get higher strength.

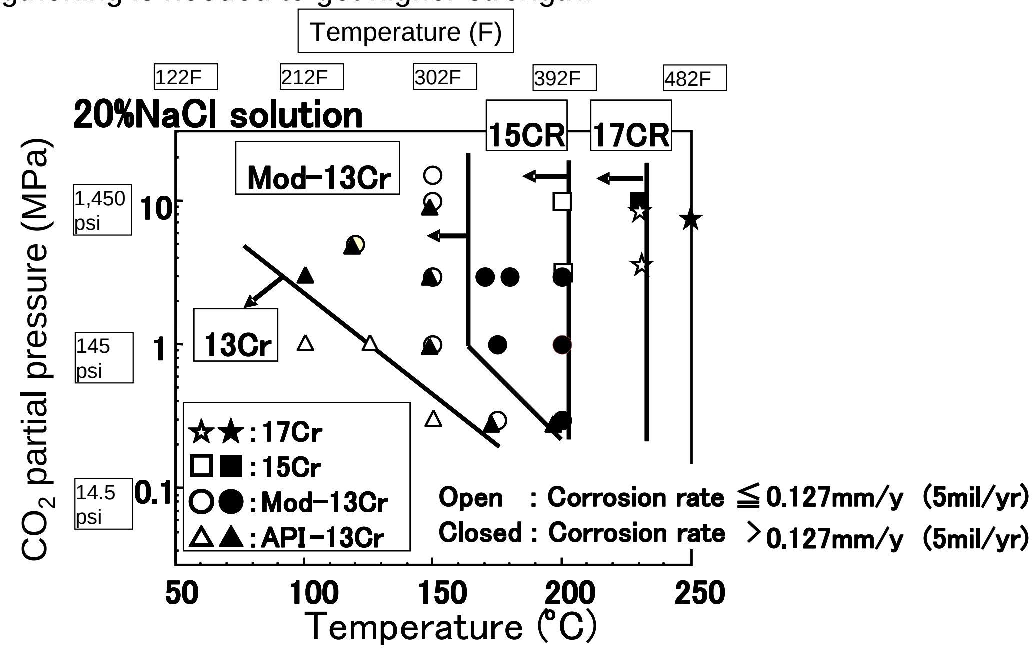


Figure 6: CO_2 corrosion resistance map in 20% NaCl solution plotted as CO_2 partial pressure and temperature in API-13Cr, Mod-13Cr, 15CR and 17CR.

As shown in Figure 5, in martensite-based 15CR and 17CR, the reduction of YS between RT and about 200 deg.C is around 100MPa, but, by contrast, in dislocation-strengthening-based 25CR, the YS sharply drops from RT to 200 deg.C. The reduction is as large as 200MPa. It is estimated cold-drawing-based dislocations in 25CR are released more easily than martensite-based strains in 15CR and 17CR.

4.4 Corrosion rate in high-pressured CO_2 corrosion

The CO_2 corrosion properties were evaluated by corrosion rate among API-13Cr, Mod-13Cr, 15CR and 17CR in 20%NaCl solution at the parameters of CO_2 partial pressure from 0.3MPa to over 10MPa and temperature form RT to 250deg.C, which targets at corrosion-resistant properties for severe sweet corrosion environment. The corrosion resistance in CO_2 corrosion was judged by using “0.127mm/year (= 5mil/year)” as the upper limits of application criteria. Figure 6 shows CO_2 corrosion rate map in API-13Cr, Mod-13Cr, 15CR and 17CR under the corrosion environment of 20% NaCl solution as parameters of CO_2 partial pressure and temperature: the former one is 0.3MPa to around 10MPa and the latter one is 100deg.C to 250deg.C. The good samples are marked as open symbols, and the bad ones are marked as solid symbols. In the order of API-13Cr, Mod-13Cr, 15CR and 17CR, which is arranged as Cr addition and corrosion-related alloy elements addition, corrosion rate is improved. When the application limits are compared under 20% NaCl solution at 10MPa of CO_2 partial pressure without any H_2S gas, Mod-13Cr, 15CR and 17CR are 165 deg.C, 200 deg.C and 230 deg.C, respectively.

4.5 SSC resistance

The SSC resistance data are shown in Figures 7-(a) to (c) for 15CR-125ksi-grade, 17CR-125ksi-grade and 17CR-110ksi-grade, respectively.
As shown in Figure 7-(a), the application limit in 15CR-125ksi-grade is expanded to lower pH and/or higher partial pressure of H_2S region when chloride ion is smaller in corrosion condition. At chloride ion of 1000ppm (=0.165%NaCl solution), SSC was not observed in pH3.5 and 0.1MPa of H_2S.
As for 17CR-125ksi-grade, Figure 7-(b) shows SSC resistance in comparison with 15CR-125ksi-grade. 17CR-125ksi-grade has better performance in SSC than 15CR-125ksi-grade, and the application limit is expanding, but still now SSC test is going on to make clear the upper limit of SSC.
In 17CR-110ksi-grade, Figure 7-(c) shows SSC performance in three different conditions of chloride ion. When chloride ion is smaller, the application limit is expanded to the lower pH and/or the higher partial pressure of H_2S. We are now doing on-going SSC tests, and at present the application limit at lower chloride condition is becoming clear with respect to whether pH value stays around 3 or smaller, and with respect to whether H_2S partial pressure is higher than 0.01MPa.

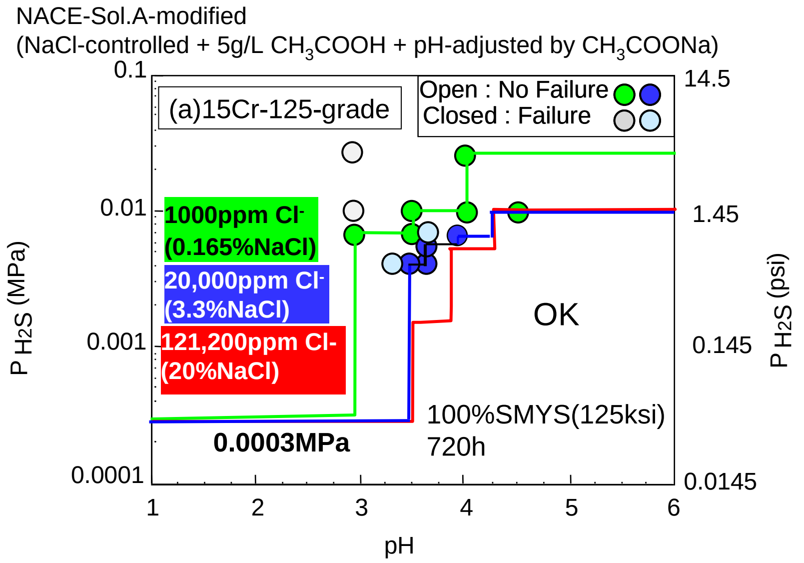
4.6 Pitting resistance

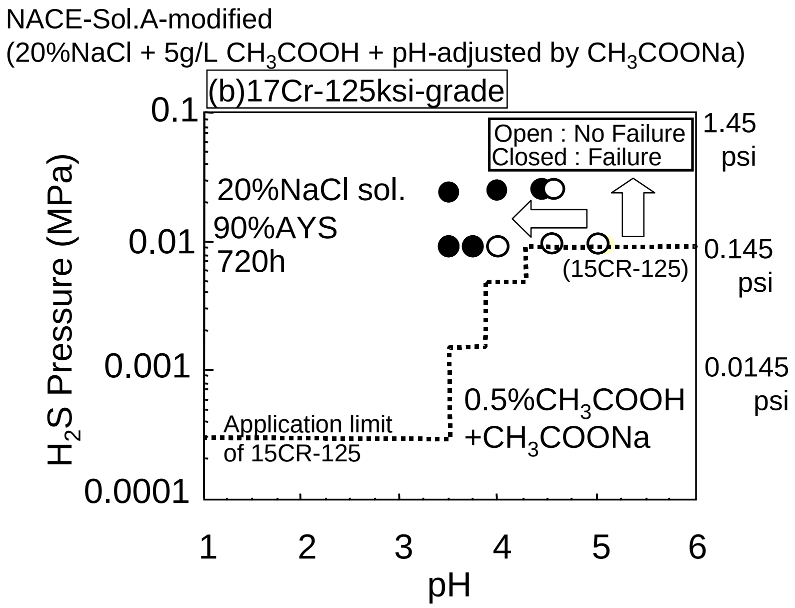
Figure 8-(a) is pitting potentials in Mod-13Cr, 15Cr and 17Cr at ambient pressure and temperature under three different corrosion conditions of “0.165%NaCl and 100%CO_2”, “20%NaCl and 100%CO_2” and “20%NaCl and 90%CO_2 + 10%H_2S”. In the order of Mod-13Cr, 15Cr and 17Cr, pitting potential is improved in each condition. Figure 8-(b) is the pitting potential of “20%NaCl and 100%CO_2” plotted against a classical pitting index of “Cr+3Mo+16N”. As pitting index is increased, the pitting

potential tends to go up. These data indicates that corrosion-resistant properties are related to the stability of passivation film.

4.7 Corrosion at low pH (acidizing simulation without inhibitors)

Figures 9-(a) and 9-(b) show corrosion rate in acidizing corrosion simulations at too low pH to exist passivation. It should be noted that the vertical axis is 2-digit to 3-digit higher in Figure 9-(a) than in Figure 9-(b), and also much higher than in Fig. 6. In any case, duplex stainless steels show worse performance in corrosion-resistance than any martensite-based stainless steels, although duplex stainless steel always shows better performance than any martensite-based stainless steels in regular corrosion environment. Figures 10-(a) to (e) are cross-sectional optical mi-





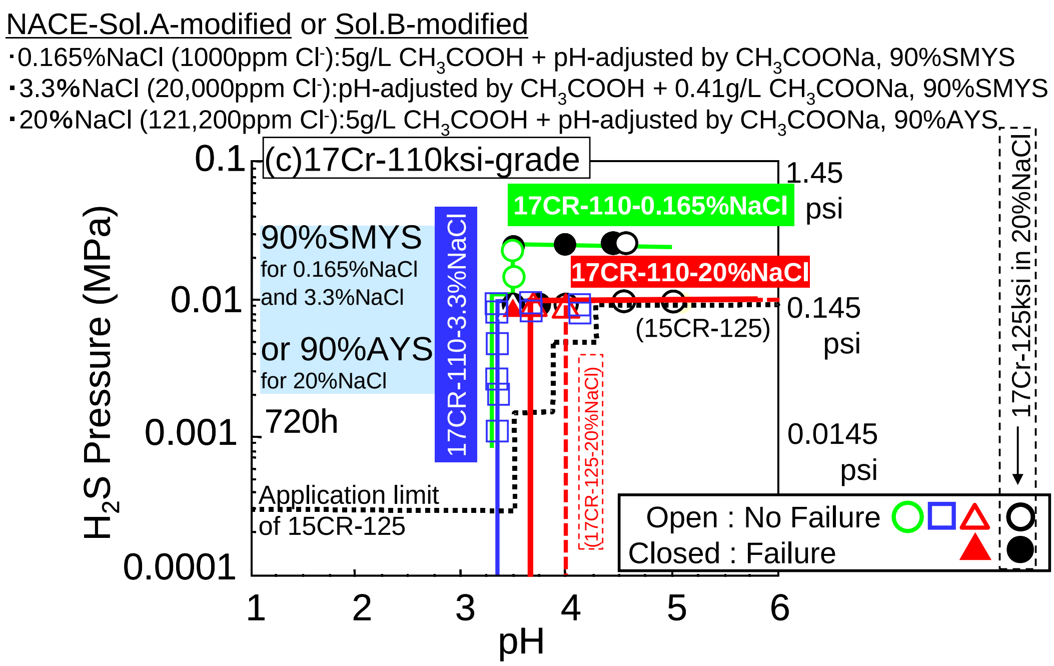


Figure 7: SSC maps in (a)15Cr-125ksi-grade, (b)17Cr-125ksi-grade and (c)17Cr-110ksi-grade.

crographs of Figure 9-(a). Mod-13Cr, 15CR and 17CR show flat surface as a whole. In contrast, selective corrosion occurs in 22Cr and 25Cr. As shown in Figures 10-(d) and 10-(e), ferrite as gray area is corroded preferentially.

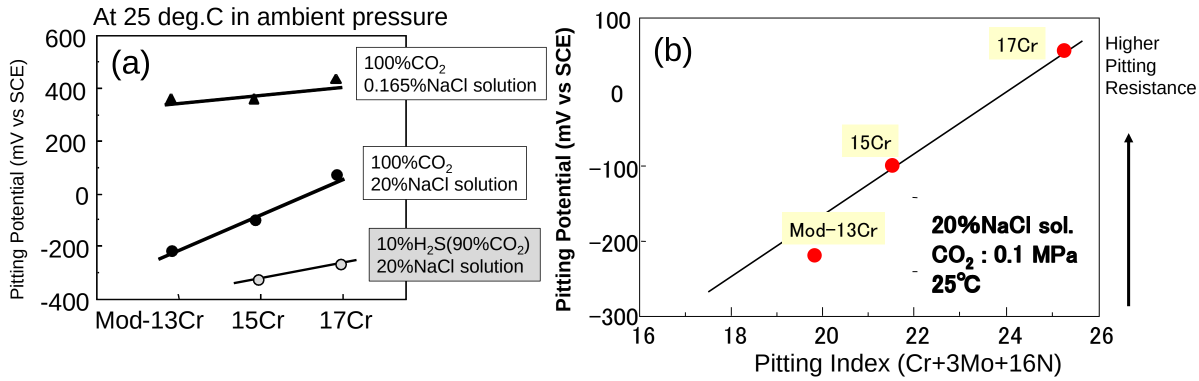


Figure 8: Passivation stability evaluation and comparison in Mod-13Cr, 15CR and 17CR by using (a) pitting potentials and (b) pitting potential – pitting index plots.

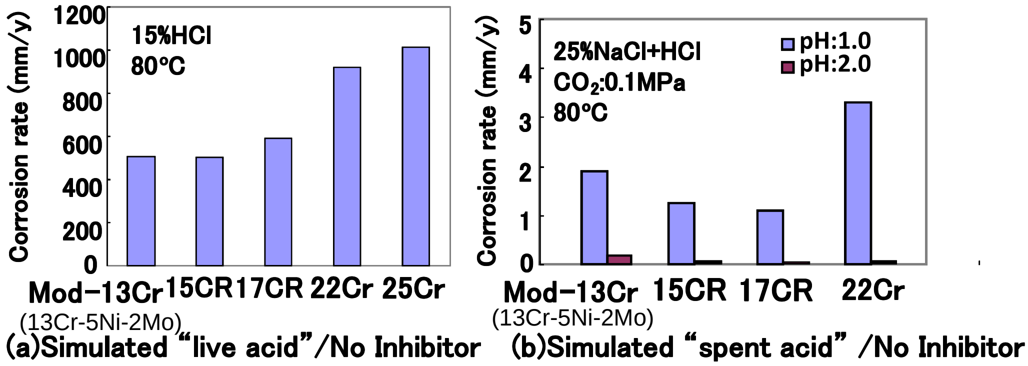


Figure 9: Low pH-based Corrosion properties (acidizing simulation without inhibitors) of (a)"live acid" simulation without inhibitors and (b) "spent acid" simulation without inhibitors.

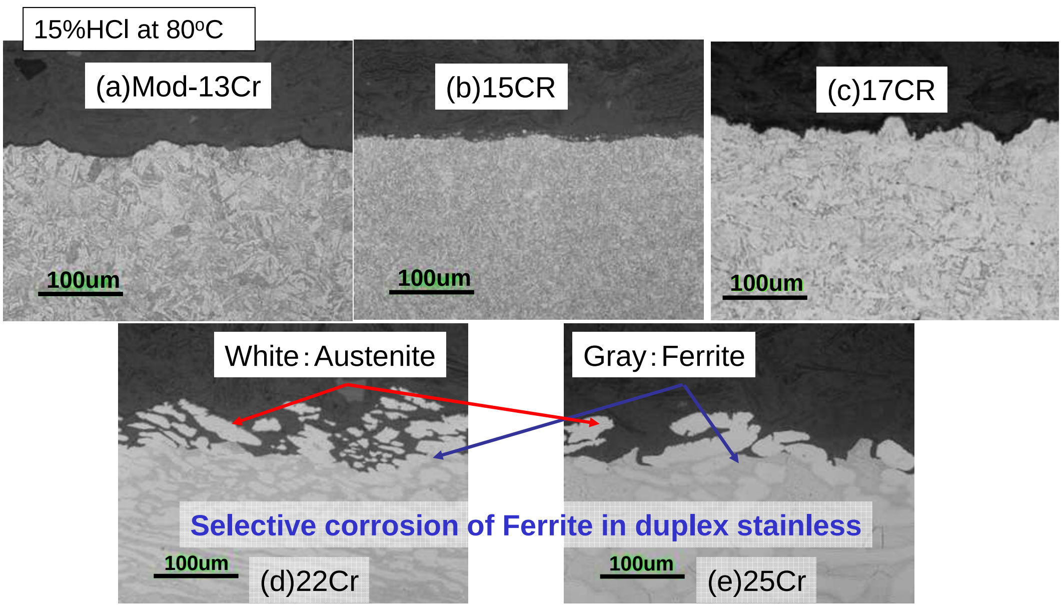


Figure 10: Cross-sectional optical micrographs of after "live acid" simulation in Figure 9-(a).

5 Discussion

In this paper, two interesting "reversal phenomena" have been shown in high-temperature strength and in acidizing-simulated corrosion properties, although most

of the properties is better in duplex stainless steel than in martensitic stainless steel. The former behavior is based on the difference of release of dislocations (strains) in martensite-including stainless steel and in cold-drawing-based duplex stainless steel. It can be explained that the dislocation in the latter is released more easily than in the former. Therefore, martensite-including stainless steels have better performance than cold-drawing-based duplex stainless steels.
The mechanism in the latter “reversal phenomenon” is discussed below. Someone might feel strange that austenite-including stainless steels have lower corrosion rate than martensite-based stainless steel in acidizing-simulated condition. The key is selective corrosion to ferrite in duplex samples. Such selective corrosion occurs on 22Cr and 25Cr, but not on 17CR. However, the potential difference in electrochemical viewpoint is needed for preferential corrosion of ferrite in ferrite–austenite (martensite) microstructure at too low pH to exist passivation film. API-13Cr, Mod-13Cr and 15CR is composed almost only of martensite. They are uniform microstructure. As for 17CR, it is based on martensite as a main phase, ferrite as a second large phase and a small portion of austenite. Duplex stainless steel is composed of austenite and ferrite. Multi-phased structure is based on elemental partitioning by mutual diffusion during production process that austenite-stabilizer elements move to austenite phase (martensite) and ferrite-stabilizer elements diffuse to ferrite phase, and then the potential difference between ferrite and austenite (martensite) occurs. The point is “high concentration” of additive elements in stainless steels. Since duplex stainless steel includes higher-concentration of elements than 17CR, the elemental partitioning in ferrite portion and in austenite (martensite) portion is more different each other than in 17CR. Therefore, it is though that selective corrosion easily occurs in ferrite area in 22Cr and 25Cr but not in 17CR despite its multi-phased steel.

5 Summary

15CR and 17CR stainless steel OCTG materials are designed to target at higher corrosion-resistant performance on the basis that main phase is martensite and strength depends on martensite but not cold-drawing-based dislocation-strengthening. The improved corrosion-resistant properties are based on the higher stability of passivation film by adding alloy elements of Cr, Ni, Mo, Cu, W and so on.
This paper has reported that 15CR and 17CR have better performances in corrosion properties and in mechanical properties than conventional martensitic stainless steel. In contrast, it can be considered appropriate that duplex stainless steels are positioned in upper grade in corrosion-resistant properties than 15CR and 17CR, but it might be possible to apply 15CR and 17CR as alternatives to the milder corrosion region in duplex-targeting corrosion environment, in addition to the application as upper grade of Mod-13Cr and API-13Cr in corrosion-resistant properties and in mechanical properties, especially one-grade-up of yield strength.

6 References

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